CLAIMS

1.   Process for the preparation of a composition comprising a vinylaromatic polymer matrix
5   surrounding rubber nodules, comprising a step of polymerizing at least one vinylaromatic monomer in the presence of a rubber, of a stable free radical which is not introduced into the polymerization mixture in a form linked to the rubber, and of a polymerization
10   initiator with a grafting character suitable for the said composition
- is such that in one of its sections at least 90% of the total area occupied by the nodules corresponds to capsules having an equivalent diameter ranging from
15   0.1 to 1 μm, or else
- is such that it comprises multi-occlusion-type nodules and is such that in one of its sections
        - 20 to 60% of the total area occupied by the particles corresponds to particles having an equivalent
20   diameter ranging from 0.1 to 1 μm,
        - 5 to 20% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 1 to 1.6 μm, and
        - 20 to 75% of the total area occupied by the
25   particles corresponds to particles having an equivalent diameter of greater than 1.6 μm.
the said step being such that:

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- if (SFR) represents the number of moles of stable free radical in the polymerization mixture,

- if F_{SFR} represents the functionality of the stable free radical, i.e. the number of sites on the same molecule of stable free radical having the stable free radical state,

- if (INIT) represents the number of moles of polymerization initiator in the polymerization mixture before phase inversion, and

- if F_{INIT} represents the functionality of the initiator introduced before phase inversion, i.e. the number of sites having the free radical state that each molecule of initiator is capable of generating, then:
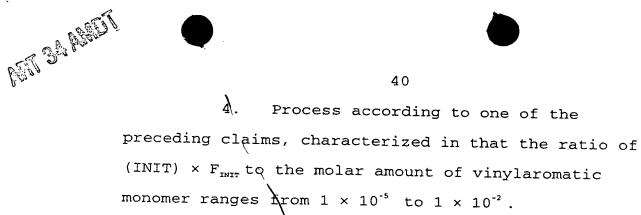
$$0.05 < \frac{F_{SFR} \times (SFR)}{F_{INIT} \times (INIT)} < 1.$$

2. Process according to the previous claim, characterized in that

$$0.05 < \frac{F_{SFR} \times (SFR)}{F_{INIT} \times (INIT)} < 0.5.$$

3. Process according to one of the preceding claims, characterized in that, if (RU) represents the number of moles of rubber,

$$0.1 < \frac{(SFR) \times F_{SFR}}{(RU)} < 10.$$

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4. Process according to one of the preceding claims, characterized in that the ratio of (INIT) $\times$ F_{INIT} to the molar amount of vinylaromatic monomer ranges from 1×10^{-5} to 1×10^{-2}.

5. Process according to one of the preceding claims, characterized in that the ratio of (INIT) $\times$ F_{INIT} to the molar amount of vinylaromatic monomer is greater than 2×10^{-4}.

6. Process according to one of the preceding claims, characterized in that the ratio of (INIT) $\times$ F_{INIT} to the molar amount of vinylaromatic monomer is greater than 4×10^{-4}.

7. Process according to one of the preceding claims, characterized in that the ratio of (INIT) $\times$ F_{INIT} to the molar amount of vinylaromatic monomer is greater than 6×10^{-4}.

8. Process according to one of the preceding claims, characterized in that the polymerization mixture during the step of the process comprises, per 100 parts by weight of vinylaromatic monomer, 2 to 35 parts by weight of rubber and 0 to 5 parts by weight of solvent.

9. Process according to one of the preceding claims, characterized in that the rubber has a weight-average molecular mass ranging from 110,000 to 350,000 and a number-average molecular mass ranging from 50,000 to 250,000, and in that the matrix of

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vinylaromatic polymer has a weight-average molecular mass ranging from 90,000 to 250,000.

10. Process according to one of the preceding claims, characterized in that the rubber nodules have partially both a salami and/or labyrinth morphology and partially both an onion and/or capsule morphology.

11. Process according to one of the preceding claims, characterized in that the composition is such that, in one of its sections,

- 20 to 60% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 0.1 to 1 µm,

- 5 to 20% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 1 to 1.6 µm, and

- 20 to 75% of the total area occupied by the particles corresponds to particles having an equivalent diameter of greater than 1.6 µm.

12. Process according to the preceding claim, characterized in that:

- in the 0.1 to 1 µm size range, more than 95% of the particles have the salami or capsule morphology,

- in the 1 to 1.6 µm size range, more than 95% of the particles have the salami morphology, and

- in the greater than 1.6 µm size range, more than 95% of the particles have the salami morphology.

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13. Process according to Claim 11, characterized in that

    - in the 0.1 to 1 μm size range, more than 95% of the particles have the capsule or onion or labyrinth morphology,

    - in the 1 to 1.6 μm size range, more than 95% of the particles have the onion or labyrinth morphology, and

    - in the greater than 1.6 μm size range, more than 95% of the particles have the labyrinth morphology.

14. Process according to one of the preceding claims, characterized in that the distribution of the equivalent diameters of nodules is bimodal.

15. Process according to one of Claims 10 to 14, characterized in that the rubber has, as a 5% by weight solution in styrene, a viscosity at 25°C ranging from 60 to 300 mPa.s.

16. Process according to one of Claims 10 to 15, characterized in that the rubber has a weight-average molecular mass ranging from 175,000 to 350,000 and a number-average molecular mass ranging from 70,000 to 250,000.

17. Process according to the preceding claim, characterized in that the rubber has a weight-average molecular mass ranging from 200,000 to 300,000

and a number-average molecular mass ranging from 90,000 to 200,000.

18. Process according to one of Claims 1 to 9, characterized in that the composition is such that, in one of its sections, at least 90% of the total area occupied by the particles corresponds to capsules having an equivalent diameter ranging from 0.1 to 1 µm.

19. Process according to the preceding claim, characterized in that the rubber has, as a 5% by weight solution in styrene, a viscosity at 25°C ranging from 15 to 60 mPa.s.

20. Process according to Claim 18 or 19, characterized in that the rubber has a weight-average molecular mass ranging from 110,000 to 200,000 and a number-average molecular mass ranging from 50,000 to 200,000.

21. Process according to the preceding claim, characterized in that the rubber has a weight-average molecular mass ranging from 150,000 to 200,000 and a number-average molecular mass ranging from 70,000 to 150,000.

22. Process according to one of the preceding claims, characterized in that the rubber is a homopolybutadiene.

23. Process according to one of the preceding claims, characterized in that the initiator is one of the following:

- isopropyl *tert*-butyl peroxycarbonate,

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- 2-ethylhexyl *tert*-butyl peroxycarbonate,

- dicumyl peroxide

- di-*tert*-butyl peroxide,

- 1,1-bis(*tert*-butylperoxy)cyclohexane,

5   - 1,1-bis(*tert*-butylperoxy)-3,3,5-

trimethylcyclohexane,

- *tert*-butyl peroxyacetate,

- cumyl *tert*-butyl peroxide,

- *tert*-butyl perbenzoate,

10   - *tert*-butyl per-2-ethylhexanoate,

- 2,2-bis(*tert*-butylperoxy)butane,

- butyl 4,4-bis(*tert*-butyl)valerate,

- ethyl 3,3-bis(*tert*-butyl)butyrate,

- 2,2-bis(4,4-di-*tert*-butylperoxycyclo-

15   hexyl)propane.

         24. Process according to one of the

preceding claims, characterized in that the initiator

is chosen from diacyl peroxides, peroxy esters, dialkyl

peroxides and peroxy acetals.

20   25. Process according to the preceding

claim, characterized in that the initiator generates at

least one *tert*-butyloxy radical.

         26. Process according to the preceding

claim, characterized in that the initiator is one of

25   the following:

- isopropyl *tert*-butyl peroxycarbonate,

- 1,1-bis(*tert*-butylperoxy)cyclohexane,

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1-1-bis(*tert*-butylperoxy)-3,3,5-trimethyl-cyclohexane.

27. Process according to one of the preceding claims, characterized in that the

5 polymerization step is carried out at least partially at 80 to 140°C.

28. Process according to one of the preceding claims, characterized in that the polymerization step is carried out at least partially

10 at 90 to 130°C.

29. Process according to one of the preceding claims, characterized in that the polymerization step is carried out at least partially, before phase inversion, at a temperature T such that

15 $T_{\mu} - 20°C < T < T_{\mu} + 20°C$, in which T_{μ} represents the temperature at which 50% of the initiator is decomposed in one hour.

30. Process according to the preceding claim, characterized in that the step is carried out at

20 least partially at a temperature T such that
$T_{\mu} - 10°C < T < T_{\mu} + 10°C$.

31. Process according to one of the preceding claims, characterized in that the polymerization initiator is added to the polymerization

25 mixture after phase inversion.

32. Process according to one of the preceding claims, characterized in that the vinylaromatic monomer is styrene.

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33. Process according to one of the preceding claims, characterized in that the polymerization is carried out continuously so that the phase inversion takes place in a plug-flow reactor.

5   34. Composition capable of being obtained by the process of one of the preceding claims.

35. Composition according to the preceding claim or comprising a stable free radical which is in a free form or in a form linked to a polymer chain by a

10   covalent bond, comprising a matrix of vinylaromatic polymer surrounding rubber nodules, characterized in that the composition comprises nodules of the multi-occlusion type and is such that, in one of its sections,

15   - 20 to 60% of the total area occupied by the particles corresponds to particles having an equivalent diameter ranging from 0.1 to 1 μm,

- 5 to 20% of the total area occupied by the particles corresponds to particles having an equivalent

20   diameter ranging from 1 to 1.6 μm, and

- 20 to 75% of the total area occupied by the particles corresponds to particles having an equivalent diameter of greater than 1.6 μm.

36. Composition according to the preceding

25   claim, characterized in that:

- in the 0.1 to 1 μm size range, more than 95% of the particles have the salami or capsule morphology,
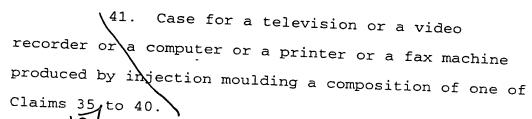
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- in the 1 to 1.6 µm size range, more than 95% of the particles have the salami morphology, and

- in the greater than 1.6 µm size range, more than 95% of the particles have the salami morphology.

37. Composition according to Claim 35, characterized in that

- in the 0.1 to 1 µm size range, more than 95% of the particles have the capsule or onion or labyrinth morphology,

- in the 1 to 1.6 µm size range, more than 95% of the particles have the onion or labyrinth morphology, and

- in the greater than 1.6 µm size range, more than 95% of the particles have the labyrinth morphology.

38. Composition according to one of Claims 34 to 37, characterized in that the distribution of the equivalent diameters of nodules is bimodal.

39. Composition according to one of Claims 34 to 38, characterized in that the melt index at 210°C with 5 kg is greater than 15 g/10 min (ISO 1133 H), the Vicat softening temperature (1 kg) is greater than 94°C (ISO 306 A50) and the notched Izod impact strength is greater than 8 kJ/m^2 (ISO 180/1A).

40. Composition according to the preceding claim, characterized in that the Vicat softening temperature (1 kg) is greater than 94.5°C and the notched Izod impact strength is greater than 9 kJ/m^2.

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41. Case for a television or a video recorder or a computer or a printer or a fax machine produced by injection moulding a composition of one of Claims 35 to 40.

5   42. Composition according to Claim 34, characterized in that the composition is such that, in one of its sections, at least 90% of the total area occupied by the particles corresponds to capsules having an equivalent diameter ranging from 0.1 to 1 μm.